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12774

# THE UNITED STATES OF AMERICA

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FILING DATE.

APPLICATION NUMBER: 60/542,569

FILING DATE: February 06, 2004

RELATED PCT APPLICATION NUMBER: PCT/US05/03792



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020604  
13142 U.S. PTO

Practitioner D K T N . TSY-001PR

PATENT

Preliminary Classification:

Proposed Class:

Subclass:

NOTE: "All applicants are requested to include a preliminary classification on newly filed patent applications. The preliminary classification, preferably class and subclass designations, should be identified in the upper right-hand corner of the letter of transmittal accompanying the application papers, for example 'Proposed Class 2, subclass 129.'" M.P.E.P., § 601, 7th ed.

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: David Tsay et al.

For: Single Stage Membrane Reactor For High Purity Hydrogen Production

Mail Stop Provisional Patent Application

Commissioner for Patents

P.O. Box 1450, Alexandria, VA 22313-1450

### COVER SHEET FOR FILING PROVISIONAL APPLICATION

(37 C.F.R. § 1.51(c)(1))

**WARNING:** "A provisional application must also include the cover sheet required by § 1.51(c)(1) or a cover letter identifying the application as a provisional application. Otherwise, the application will be treated as an application filed under paragraph (b) [nonprovisional application] of this section." 37 C.F.R. § 1.53(c)(1). See also M.P.E.P. § 201.04(b), 6th ed., rev. 3.

#### EXPRESS MAILING UNDER 37 C.F.R. § 1.10\*

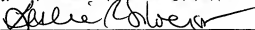
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Leslie R. Silverstein

(type or print name of person mailing paper)



Signature of person certifying

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(Cover Sheet for Filing Provisional Application [23-1]—page 1 of 5)

22154 U.S. PTO  
60/542569  
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- NOTE: "A complete provisional application does not require claims since no examination on the merits will be given to a provisional application. However, provisional applications may be filed with one or more claims as part of the application. Nevertheless, no additional claim fee or multiple dependent claims fee will be required in a provisional application." Notice of December 5, 1994, 59 Fed. Reg. 63,951, at 63,953. "Any claim filed with a provisional application will, of course, be considered part of the original provisional application disclosure." Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,209.
- NOTE: "A provisional application is not entitled to the right of priority under 35 U.S.C. 119 or 365(a) or § 1.55, or to the benefit of an earlier filing date under 35 U.S.C. 120, 121 or 365(c) or § 1.78 of any other application. No claim for priority under § 1.78(a)(3) may be made in a design application based on a provisional application. No request under § 1.293 for a statutory invention registration may be filed in a provisional application. The requirements of §§ 1.821 through 1.825 regarding application disclosures containing nucleotide and/or amino acid sequences are not mandatory for provisional applications." 37 C.F.R. § 1.53(c)(3).
- NOTE: "No information disclosure statement may be filed in a provisional application." 37 C.F.R. § 1.51(d). "Any information disclosure statements filed in a provisional application would either be returned or disposed of at the convenience of the Office." Notice of December 5, 1994, 59 Fed. Reg. 63,591, at 63,594.
- NOTE: "No amendment other than to make the provisional application comply with the patent statute and all applicable regulations may be made to the provisional application after the filing date of the provisional application." 37 C.F.R. § 1.53(c).
- NOTE: 35 U.S.C. 119(e)(1) requires that a nonprovisional application be filed within twelve months of the filing date of the provisional application for the nonprovisional application to claim the benefit of the filing date of the provisional application. Under 35 U.S.C. 21(b) and 119(e)(3), if this twelve-month period expires on a non-business day, it is extended to expire on the next business day.

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.51(c)(1)(i).

1. The following comprises the information required by 37 C.F.R. § 1.51(c)(1):
2. The name(s) of the inventor(s) is/are (37 C.F.R. § 1.51(c)(1)(i)):

NOTE: "If the correct inventor or inventors are not named on filing a provisional application without a cover sheet under § 1.15(c)(1), the later submission of a cover sheet under § 1.15(c)(1) during the pendency of the application will act to correct the earlier identification of inventorship." 37 C.F.R. § 1.48(f)(2).

NOTE: "The naming of inventors for obtaining a filing date for a provisional application is the same as for other applications. A provisional application filed with the inventors identified as 'Jones et al.' will not be accorded a filing date earlier than the date upon which the name of each inventor is supplied unless a petition with the fee set forth in § 1.17(f) is filed which sets forth the reasons the delay in supplying the names should be excused. Administrative oversight is an acceptable reason. It should be noted that for a 35 U.S.C. 111(a) application to be entitled to claim the benefit of the filing date of a provisional application the 35 U.S.C. 111(a) application must have at least one inventor in common with the provisional application." Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,209.

The term "invention" is typically used to refer to subject matter which applicant is claiming in his/her application. Because claims are not required in a provisional application, it would not be appropriate to reference joint inventors as those who have made a contribution to the "invention" disclosed in the provisional application. If the "invention" has not been determined in the provisional application because no claims have been presented, then the name(s) of those person(s) who have made a contribution to the subject matter disclosed in the provisional application should be submitted. Section 1.45(c) states that "if multiple inventors are named in a provisional application, each named inventor must have made a contribution, individually or jointly, to the subject matter disclosed in the provisional application." All that § 1.45(c) requires is that if someone is named as an inventor, that person must have made a contribution to the subject matter disclosed in the provisional application. When applicant has determined what the invention is by the filing of the 35 U.S.C. 111(a) application, that is the time when the correct inventors must be named. The 35 U.S.C. 111(a) application must have an inventor in common with the provisional application in order for the 35 U.S.C. 111(a) application to be entitled to claim the benefit of the provisional application under 35 U.S.C. 119(e). Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,208.

See 37 C.F.R. § 1.53.

- |    |                   |  |
|----|-------------------|--|
| 1. | <u>David</u>      | <u>Tsay</u>  |
|    | <u>GIVEN NAME</u> | <u>MIDDLE INITIAL OR NAME</u> <u>FAMILY (OR LAST) NAME</u> |
| 2. | <u>Steven</u>     | <u>E.</u> <u>Weiss</u>                                     |
|    | <u>GIVEN NAME</u> | <u>MIDDLE INITIAL OR NAME</u> <u>FAMILY (OR LAST) NAME</u> |
| 3. | <u></u>           | <u></u> <u></u>  |
|    | <u>GIVEN NAME</u> | <u>MIDDLE INITIAL OR NAME</u> <u>FAMILY (OR LAST) NAME</u> |

3. Residence address(es) of the inventor(s), as numbered above (37 C.F.R. § 1.51(c)(1)(iii)):

1. 10 Walnut Street, #PH, Boston, MA 02108
2. 1 Fifth Street, Cambridge, MA 02142
3.

4. The title of the invention is (37 C.F.R. § 1.51(c)(1)(iv)):

Single Stage Membrane Reactor For High Purity Hydrogen Production

5. The name, registration, customer and telephone numbers of the practitioner (if applicable) is (37 C.F.R. § 1.51(c)(1)(v)):

Name of practitioner: David Silverstein

Reg. No. 26,336 Tel. (978) 470-0990

Customer No.

*(complete the following, if applicable)*

☐ A power of attorney accompanies this cover sheet.

6. The docket number used to identify this application is (37 C.F.R. § 1.51(c)(1)(vi)):

Docket No.: TSY-001PR

7. The correspondence address for this application is (37 C.F.R. § 1.51(c)(1)(vii)):

David Silverstein

Andover-IP-Law, 44 Park Street, Suite 300, Andover, MA 01810

8. Statement as to whether invention was made by an agency of the U.S. Government or under contract with an agency of the U.S. Government.  
(37 C.F.R. § 1.51(c)(1)(viii))

This invention was made by an agency of the United States Government, or under contract with an agency of the United States Government.

☒ No.

☐ Yes.

The name of the U.S. Government agency and the Government contract number are:

9. Identification of documents accompanying this cover sheet:

A. Documents required by 37 C.F.R. §§ 1.51(c)(2)-(3):

Specification: (incl. cover page)

No. of pages 15

Drawings:

No. of sheets 3

B. Additional documents:

☒ Claims:

No. of claims 14

Note: See 37 C.F.R. § 1.51.

☐ Power of attorney

☒ Small entity assertion

☐ Assignment

☐ English language translation of non-English provisional application

NOTE: A provisional application which is filed in a language other than English, does not have to have an English language translation. See 37 C.F.R. § 1.52(d)(2). However, if the provisional application is not in the English language and will later serve as a benefit of its filing date for a nonprovisional application, other than a design patent, or for an international application designating the U.S., then an English language translation must be filed in the provisional application or the later filed nonprovisional application. See § 1.78(a)(5)(iv).

☐ This application is in a language other than English and an English translation along with a statement of its accuracy is submitted herewith.

☒ Other - Abstract (1 page)

10. Fee

The filing fee for this provisional application, as set in 37 C.F.R. § 1.16(k), is \$160.00, for other than a small entity, and \$80.00, for a small entity.

☒ Applicant is a small entity.

NOTE: "A . . . statement in compliance with existing § 1.27 is required to be filed in each provisional application in which it is desired to pay reduced fees." Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,197.

11. Small entity assertion

☐ The assertion that this is a filing by a small entity under 37 C.F.R. § 1.27(c)(1) is attached. ("ASSERTION OF SMALL ENTITY STATUS")

☒ Small entity status is asserted for this application by payment of the small entity filing fee under § 1.16(k). 37 C.F.R. § 1.27(c)(3).

12. Fee payment

☒ Fee payment in the amount of \$ 80.00 is being made at this time.

☐ No filing fee is to be paid at this time. (This and the surcharge required by 37 C.F.R. 1.16(l) can be paid subsequently).

13. Method of fee payment

- ☒ Attached is a ☒ check ☐ money order in the amount of \$ 80.00  
☒ Authorization is hereby made to charge ~~this amount to~~ any fee deficiency  
☒ to Deposit Account No. 50-1139  
☐ to Credit card as shown on the attached credit card information authorization form PTO-2038.

**WARNING:** Credit card information should not be included on this form as it may become public.

- ☒ Charge any additional fees required by this paper or credit any overpayment in the manner authorized above.

A duplicate of this paper is attached.

Date: \_\_\_\_\_

Tel.: (      )


Date: Feb 6, 2004

Reg. No.: 26,336

Tel.: ( 978 ) 470-0990

Customer No.:

\_\_\_\_\_  
Signature of submitter

OR  
  
\_\_\_\_\_  
Signature of practitioner

\_\_\_\_\_  
David Silverstein  
(type or print name of practitioner)

\_\_\_\_\_  
Andover-IP-Law  
\_\_\_\_\_  
P.O. Address  
44 Park Street, Suite 300  
\_\_\_\_\_  
Andover, MA 01810

PROVISIONAL

APPLICATION

FOR

UNITED STATES LETTER PATENT

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SPECIFICATION

TO ALL WHOM IT MAY CONCERN:

Be it known that David Tsay of Boston, Massachusetts and Steven E. Weiss of Cambridge, Massachusetts have invented certain improvements in SINGLE STAGE MEMBRANE REACTOR FOR HIGH PURITY HYDROGEN PRODUCTION of which the following description is a specification.



## **SINGLE STAGE MEMBRANE REACTOR FOR HIGH PURITY HYDROGEN PRODUCTION**

### **FIELD OF INVENTION**

This invention relates generally to a hydrogen manufacturing process and to related apparatus utilizing a catalyst-coated protonic-electron conducting cermet membrane to form a one-stage fuel reforming, water-gas-shift, and hydrogen purification system.

### **BACKGROUND OF THE INVENTION**

Hydrogen forming reaction systems, such as steam/methane reforming (wherein methane and water are reacted to form carbon monoxide), and carbon dioxide and hydrogen and water-gas-shift reaction systems (wherein carbon monoxide is reacted with water to form carbon dioxide and hydrogen), are well known to the art.

Steam/methane reforming is typically used as a catalytic reaction system for the production of hydrogen. Conventional catalytic systems for steam/methane reforming require primary catalytic reaction temperatures on the order of 1200 degrees F. and above, followed by rather extensive and expensive purification processes to provide a hydrogen product suitably pure to be used as a feed stock for many common processes. Catalytic steam/methane reforming processes as currently used are summarized in Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Vol. 12, John Wiley & Son, pages 944, 950-95, which is incorporated herein by reference.

The water-gas-shift reaction is an alternative hydrogen production technology frequently used following the primary catalytic reaction to remove carbon monoxide impurities and increase hydrogen yield. The water-gas-shift reaction is mildly exothermic and thus is thermodynamically favored at lower temperatures. However, the kinetics of the reaction are superior at higher temperatures. Thus, it is common practice to first cool the reformat product from the steam reformer in a heat exchanger to a temperature between about 350 degrees C. and 500 degrees C., and then to conduct the reaction over a catalyst composed of finely divided oxides of iron and chromium formed into tablets. The resulting reformat gas is then cooled once again to a temperature between about 200 degrees C. and 250 degrees C. and reacted over a catalyst based upon mixed oxides of copper and nickel. A review of current applications and processes for such water-gas-shift reactions is found in Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Vol. 12, John Wiley & Sons, pages 945, 951-952, which is incorporated herein by reference.

It is also known to use hydrogen ion conductive metal foils or molecular hydrogen permeable metal membranes to withdraw hydrogen in situ from the hydrogen forming reaction to permit the use of higher temperatures and the higher yielding water-gas-shift reaction, as described for example in U.S. Pat. No. 4,810,485, U.S. Pat. No. 5,997,597 and U.S. Pat. No. 6,033,634, which are incorporated herein by reference. These patents teach the use of hydrogen transport metal foils or porous metallic membranes for separating and conducting hydrogen in contact with and independent of the catalytic reaction system, but they do not describe or suggest a process or apparatus

capable of integrating the reforming reaction, water-gas-shift reaction, and gas purification into a coordinated unitized system.

The use of dense protonic ceramic membranes for hydrogen separation and purification is also known in the art. For example, U.S. Pat. No. 6,296,687, U.S. Pat. No. 6,235,417 and U.S. Pat. No. 5,821,185, which are incorporated herein by reference, describe the use of single-phase and mixed-phase perovskite-type oxidic protonic ceramic membranes for separating or decomposing hydrogen-containing gases or other such compounds to yield higher value products, but they do not describe or suggest a process or apparatus comprising a one-step hydrocarbon to hydrogen reforming reaction, water-gas-shift reaction, and gas purification combined and efficiently integrated into a unitized system. The teachings of these patents also do not describe or suggest methods to lower the sintering temperature of the protonic ceramic membrane to allow for lower manufacturing costs. These and other deficiencies in or limitations of the prior art are overcome in whole or at least in part by the single stage membrane reactors and related methods of this invention.

#### OBJECTS OF THE INVENTION

Accordingly, it is a principal object of this invention to integrate a reformation catalyst and protonic-electron conduction cermet membrane into a hydrogen forming reaction system to promote hydrogen generation and to facilitate withdrawal in situ of such produced hydrogen.

Another object of this invention is to provide a reformation reaction adapted for in situ withdrawal of hydrogen to improve the water-gas-shift and reforming reaction equilibrium.

Yet another object of this invention is to provide hydrogen forming reaction processes which produce substantially pure hydrogen without the need for conventional water-gas-shift and chemical purification systems.

It is still another object of this invention to provide a water-gas-shift hydrogen forming reaction system adapted to operate efficiently at higher temperatures than conventional water-gas-shift reaction processes.

Still another object of this invention is to provide a membrane reactor support design and related enclosure structure which facilitates high pressure operation and affords the ability to utilize thin catalyst-membrane subassemblies.

A further object of this invention is to provide a method for protonic-electron conducting cermet membrane fabrication that is compatible with silicon carbide element furnaces by lowering the sintering temperature to about 1500 degrees C.

These and other objects, advantages and benefits of this invention will be better understood by the following description read in conjunction with Figs. 1A and 1B and Figs. 2A, 2B and 2C.

## SUMMARY OF THE INVENTION

The present invention relates generally to a solid state membrane reactor for producing high purity hydrogen by reacting an alcohol or a hydrocarbon feed with steam in the presence of catalyst and thereafter withdrawing the hydrogen produced in situ from the reaction zone through a protonic-electron conducting cermet membrane in accordance with this invention. The cermet membrane of this invention is made from a first phase of proton-conducting ceramic material of the perovskite compound and a secondary phase of electron-conducting metallic material. The secondary phase of metallic additive also functions as a sintering aid to lower the fabrication temperature of the cermet membranes of this invention. The cermet membranes of this invention preferably include a reformation catalyst surface. The catalyst-membrane subassembly is encased in high temperature sustainable shells that incorporate designs to provide sealing, manifolding, expansion support, alternating semi-permeable and non-permeable regions to facilitate the separation of a plurality of reaction and resultant chambers, delivery of pressurized reformation feedstock, support of the membrane, and withdrawal of product gas. A plurality of the said unitized membrane assemblies is accumulated to form a reactor stack in accordance with this invention.

As part of this invention, it has been found that it is possible to utilize a material that provides both the requisite electronic conductivity while acting as the sintering aid during processing. In particular, it is a preferred embodiment of this invention to utilize relatively low melting point transition metals such as copper (Cu) and cobalt (Co). These materials when properly dispersed at levels of about 1-20 wt%, preferably 5-10 wt%,

have been found to act as a liquid phase sintering aid and to provide the necessary electric conductivity to produce a composite mixed conducting cermet membrane in accordance with this invention at a lower than usual sintering temperature of about 1400-1600 degrees C., preferably about 1450 degrees C.

A process for reforming, shifting and purifying alcohol or hydrocarbon feedstocks, for example, can be advantageously carried out using a membrane reactor in accordance with the present invention. Such a process would typically comprise the sequential steps of:

- a) heating the membrane reactor or reactor stack to a temperature from about 1100 degrees F. to about 1800 degrees F. and, more preferably, to about 1300 degrees F.;
- b) passing a feedstock and water vapor to a reformation side of the mixed conducting cermet membrane at elevated pressure;
- c) withdrawing hydrogen through the mixed conducting cermet membrane to the lower pressure outlet side;
- d) releasing hydrogen to a collection tank through a pressure-sensitive release valve; and,
- e) combusting the reformation purge stream to yield supplemental heat for the membrane reactor or reactor stack.

Based on the forgoing, a number of advantages are realized with the process and apparatus of the present invention including:

- 1) single integrated and coordinated process and apparatus for the various reforming, shifting and purifying reactions;
- 2) requires no cooling down of intermediate product gas for shifting and purifying reactions;
- 3) only one catalyst or catalytic surface is necessary;
- 4) cermet membrane can be made very thin for higher permeation performance at least in part because it is structurally sustained by the expansion foil and shell enclosures;
- 5) hydrogen purity is optimized;
- 6) compact size and energy efficient.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Fig. 1A is a schematic sectional side view of a membrane reactor subassembly according to the present invention.

Fig. 1B is a schematic sectional side view of a membrane/catalyst unit according to the present invention.

Fig. 2A is a schematic sectional side view of a disassembled multicomponent membrane reactor stack according to the present invention.

Fig. 2B is a schematic right (interior) end view of the left end terminating cap unit seen in Fig. 2A.

Fig. 2C is a schematic end view of one of the several membrane/catalyst units shown in Fig. 2A as viewed from the catalyst layer side.

## DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention discloses a process and apparatus wherein a protonic-electron conducting cermet membrane reactor is used to thermal-catalytically dissociate a reformation hydrocarbon feedstock to hydrogen-containing gas together with continuously withdrawing the hydrogen produced in situ to promote the reformation and shifting reactions. The cermet membrane of this invention is preferably made of a perovskite ceramic oxide phase represented generally by the chemical formula:  $ABO_3$  where A is preferably selected from the group of metals consisting of Ba, Ca, Mg and Sr, and B is selected from the group consisting of the class of compounds having the general chemical formula  $Ce_{1-x-y}Zr_xM_y$ , where  $0 \leq x \leq 0.6$ ,  $0 \leq y \leq 0.2$ , and M is an element selected from the group consisting of Y, Yb, In, Gd, Nd, Eu, Sm and Tb, in combination with a electron conductor metal phase comprising palladium, nickel, cobalt, iron, ruthenium, rhodium, osmium, iridium, platinum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, copper, silver, gold, and alloys thereof, preferably palladium, copper/nickel and palladium/silver alloys. The cermet membrane as described above is preferably coated with a catalyst layer selected from the group consisting of palladium, nickel, cobalt, iron, ruthenium, rhodium, osmium, iridium, platinum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, copper, silver, gold, and mixtures thereof, preferably nickel or copper/nickel. For some embodiments of this invention, the catalyst may be further doped with a perovskite ceramic oxide.

Referring now to the drawings, single-cell and multiple-cell cermet membrane reactors according to the present invention are schematically represented in Figs. 1A and



1B and Figs. 2A, 2B, and 2C, respectively, and are described below in connection with the Example.

#### Example 1

In a preferred embodiment of this invention, protonic ceramic powder consisting essentially of  $\text{BaCe}_{0.5}\text{Zr}_{0.4}\text{Y}_{0.1}\text{O}_3$  composition is made using combustion synthesis or chemical precipitation methods. Cupric nitrate is then impregnated into the ceramic powder to reach incipient wetness, typically at a level of about 5 weight % of Cu in the blend. The impregnated powder is then calcined at about 300 °C for about 10 hours. The calcined powder is then blended with suitable binders (such as polyvinyl butyral, B-79), plasticizers (such as butyl benzyl phthalate, S-160), dispersants (such as polyester /polyamide copolymer, KD-1) and solvents (such as combinations of isopropyl alcohol and toluene) and milled for about 12 hours to form a slurry. The slurry is de-aired and pumped into the reservoir of a tape casting machine, where it is casted onto a mylar sheet to form a green tape upon curing of about 0.004 in (0.1 mm) in thickness. The tape is trimmed to desired dimension by mechanical or thermal blanking. The blanked tape is then placed onto a firing setter and sintered in air at about 1450 °C for about 3 hours. The sintered cermet membrane 2 as shown in the Figures is then thinly coated with about 0.002 in (0.05 mm) of porous nickel catalyst paste 1 using a screen printer. The catalyst coated membrane is placed in an air furnace and further sintered at about 1200 °C for about 1 hour.

The shell container 9 as shown in the Figures is designed with manifolds 8, semi-permeable region 6 and non-permeable region 5, as seen schematically in Figs. 1A, 2A and 2B, is fabricated and machined from type 304 stainless steel. The expansion foil 4

may be selected, for example, from one of the non-woven foil product lines commercially available from Delker Corp., and is trimmed to size. The sealant **3 and 7** may be selected, for example, from one of the group of higher temperature glass sealant pastes commercially available from Ferro Corp or ceramic-metal adhesives from Cotronics Corp. The assembly of the membrane reactor according to this invention is completed by inserting the expansion foil into the middle of the shell container. Glass or ceramic-metal sealant paste is applied to the perimeter of the expansion foil and the shell container. The catalyst-membrane subassembly is affixed to the top of the expansion foil where it is held in position by the sealant. The matching shell container is positioned and affixed to the assembled shell container and is also held in place by the sealant. The assembled single-cell membrane reactor is then placed into an air furnace and brought up to about 800 °C for about 10 minutes, and thereafter cooled slowly. Multiple-cell membrane reactor units in accordance with this invention may be fashioned by stacking a plurality of the individual shell assemblies **9, 10, 11, and 12**.

It will be apparent to those skilled in the art that changes and modifications may be made in the above-described apparatus and process for a single-stage membrane reactor for high purity hydrogen production without departing from the spirit and scope of the invention herein, and it is intended that all matter contained in the above description shall be interpreted in an illustrative and not a limiting sense.

Having described the invention, what is claimed is:

CLAIMS

1. A membrane reactor, comprising:  
a reformation chamber containing a porous layer of reformation catalyst which is supported by and adhered to a dense protonic-electron conducting cermet membrane, wherein the reformation chamber is adapted to receive reformation feedstock and produce a reformat stream including hydrogen; and wherein molecular hydrogen of the reformat stream are dissociated into ionic hydrogen by the said reformation catalyst and conducted to the other side by the protonic-electron conducting cermet membrane; and  
the hydrogen ions are reconstituted into molecular hydrogen with the supply of electrons.
2. A membrane reactor of claim 1 wherein the operating temperature is raised to and maintained at between 1100.degree.F. to 1800.degree.F by an integral fuel burner, fuel oxidizer, electric heater, or imported heat stream. .
3. A membrane reactor of claim 1 wherein the reformation feedstock is compressed to above ambient pressure.
4. A membrane reactor of claim 1 wherein the protonic-electron conducting cermet material consists of a proton conducting ceramic phase represented by the formula:  $ABO_3$  where A is selected from the group consisting of Ba, Ca, Mg and Sr and B is  $Ce_{1-x-y}Zr_xM_y$  where  $0 \leq x \leq 0.6$ ,  $0 \leq y \leq 0.2$  and M is an element selected from the group

consisting of Y, Yb, In, Gd, Nd, Eu, Sm and Tb,, and a metal phase consisting of Ru, Rh, Pd, Ir, Pt, Re, Ni, Cu, Co or a mixture thereof.

5. A membrane reactor of claim 4 wherein the metal phase additive also functions as sintering aid.
6. A membrane reactor of claim 1 wherein the reformation catalyst is selected from the group consisting of palladium, nickel, cobalt, iron, ruthenium, rhodium, osmium, iridium, platinum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, copper, silver, gold and mixture thereof.
7. A reformation catalyst of claim 6 wherein the selected metal catalyst may be additionally blended with single-phase mixed metal oxide proton conducting material.
8. A reformation catalyst of claim 6 or 7 wherein the catalyst layer is deposited or sintered onto the cermet membrane.
9. A membrane reactor of claim 8 wherein the catalyst-membrane subassembly is encased between two metallic, ceramic or cermet containment shells.
10. A membrane reactor of claim 9 wherein the each shell includes o-rings, seals, gaskets or brazes at the inner cavity edge and outer shell edge, a semi-permeable support

region with an expansion foil in the center, and a non-permeable parameter that includes manifold ports.

11. A membrane reactor of claim 10 wherein a plurality of shells, each containing a catalyst-membrane subassembly in the cavity and sealed or adhered to the shell to separate the reformation and resultant chambers, are bonded hermetically to form a stack that is encased with two terminal shells.
12. A membrane reactor of claim 11 wherein the manifolds of the reformation chambers are hermetically joined to the fuel feed and purged exhaust conduit.
13. A membrane reactor of claim 11 wherein the manifolds of the resultant chambers are hermetically joined to the product gas withdraw conduits.
14. A membrane reactor of claim 13 wherein the purged reformation stream is diverted to the heating source to be combusted and produce heat for the membrane reactor.

ABSTRACT OF THE DISCLOSURE

A hydrogen generating process and apparatus is disclosed wherein one side of a mixed phase protonic-electron conducting cermet membrane is coated with porous metal or composite catalyst to decompose hydrocarbon and water reactants into hydrogen-rich syngas at elevated temperature and pressure and further wherein hydrogen ions are continuously withdrawn in situ by the mixed conducting cermet membrane to the opposing side and reconstituted into molecular hydrogen with the supply of electrons. This invention is particularly advantageous in favorably shifting the equilibrium of steam reforming and water-gas shift reactions to provide a single stage, high efficiency and high purity hydrogen membrane reactor.

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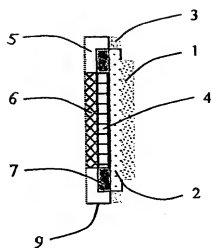


Figure 1A

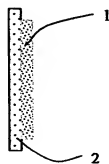


Figure 1B

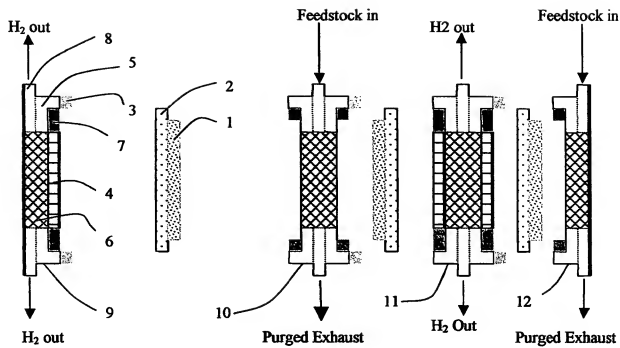


Fig. 2A



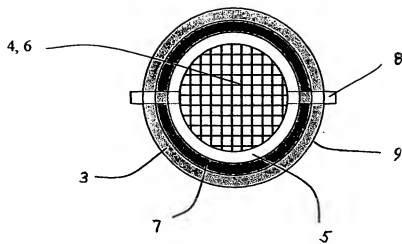


Fig. 2B

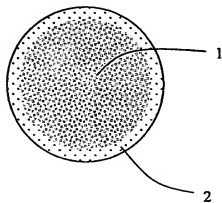


Fig. 2C

## IN THE UNITED STATES PATENT AND TRADEMARK OFFI E

In re application of: David Tsay et al.

☒ Application No.: 60 /☒ Filed herewith

For: Single Stage Membrane Reactor for High Purity Hydrogen Production

## POWER OF ATTORNEY FOR PROVISIONAL APPLICATION

Each inventor, identified above and signing below, hereby appoints the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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Inventor(s)

Signature

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Date: _____	_____	_____
Date: _____	_____	_____